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Japan Patent Office (JP)

I.S.# 181

Public Report of Opening of the Patent

Opening No. of patent: H 5-178794

Date of Opening: July 20, 1993

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269/02		6917-4H	
271/16		6917-4H	
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Date of application: Dec. 26, 1991

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Detailed Report.

Name of the invention:

bi-functional (metha)acrylate

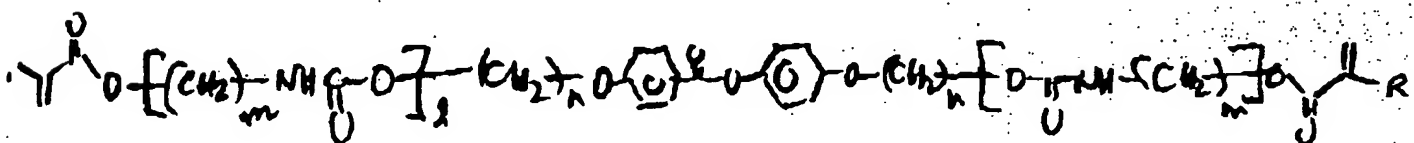
Outline

(object)

This invention supplies a new radical polymerizing bi-functional (metha)acrylate.

(constitution)

This invention is regarding a bi-functional (metha)acrylate which is expressed by the general formula on page 1. (In the formula, R₁ is H or CH₃, l is 0 or 1, m is 2 to 4, n is 2 to 12)



Sphere of the patent application
(requested clause 1)

This invention is regarding a bi-functional (metha)acrylate which is expressed by the general formula on page 2). (In the formula, R_1 is -H or -CH₃, l is 0 or 1, m is 2 to 4, n is 2 to 12)

(field of industrial use)

This invention is regarding a new radical polymerizing bi-functional (metha)acrylate.

(prior art)

Formerly, various multifunctional (metha)acrylates for polymers or co-polymers has been known. For instance, aliphatic (metha)acrylates such as hexandiol (metha)acrylate, neopentyl glycol di(metha)acrylate, polyethylen glycol di(metha)acrylate, polypropylene glycol di(metha)acrylate, glycerol tri(metha)acrylate, trimethylol propane tri(metha)acrylate, penta erythritol tri(metha)acrylate, dipenta erythritol hexa(metha)acrylate; or aromatic (metha)acrylate such as bisphenol A glycidyl di(metha)acrylate, ethylene oxide denatured bisphenol A di(metha)acrylate are public knowledge.

These kinds of aliphatic or aromatic (metha)acrylates are generally used for crosslinking material of various high molecular weight materials for electronic parts, optical materials, and ~~plastic materials~~. However, although aliphatic (metha)acrylate is generally superior in polymerization, its polymerization has problems such as it is not strong or durable is not sufficient. On the other hand, aromatic (metha)acrylate polymer is better in these characteristics compared to (metha)acrylate, but it is still not enough.

(problems that this invention tries to solve)

The object of this invention is to supply a polymer which is superior in both strength and durability.

(steps for solving the problems)

That is, this invention is regarding bi-functional (metha)acrylate which is expressed by the general formula (I) on page 2 (In the formula, R_1 is -H or -CH₃, l is 0 or 1, m is 2 to 4, n is 2 to 12)

general formula (I)

The (metha)acrylate of this invention is expressed by the general formula (I), but as a more specific example of an especially good example, there are the following compounds.

see formula on page 3

(a) infrared absorption spectrum (IR)

Generally, in (metha)acrylate ester, absorption based on the carbonyl group around 1720 cm^{-1} can be observed. Also, absorption due to a double bond is observed at 1640 cm^{-1} . Absorption of the carbonyl group bonded directly to the phenyl group is observed at 1730 cm^{-1} , and absorption of the phenyl group can be observed around 160 cm^{-1} . Also, the absorption of the carbonyl group due to $-\text{NH}-\text{C}(\text{O})\text{C}-$ is observed at 1630 to 1700 cm^{-1} .

(b) ^1H nuclear magnetic resonance spectrum

By the chemical shift of ^1H , the generated substance can be identified. Regarding specific identification of the compound of this invention, it will be explained in the following example of practice. However, the compound of this invention can be identified by ^1H nuclear magnetic resonance spectrum.

(c) mass spectrum

Using field ion-mass spectroscopy, the molecule ion peak M^+ of compound of this invention can be confirmed.

(d) element analysis

Regarding the identification of the compound of this invention, more detailed identification will be possible by either the ^1H nuclear magnetic resonance spectrum or by comparing the result of each elemental analysis of the obtained compound and the theoretical calculated values for H, C, N and in the compound.

Therefore, the bi-functional (metha)acrylate of this invention can be identified using the analysis methods stated in the above (a) to (d).

The manufacturing method of the bi-functional (metha)acrylate of this invention is not limited to any specific method - it can be any method. A representative manufacturing method is going to be explained in the following.

An alcohol halide expressed by general formula (1): $\text{X}-(\text{CH}_2)_n-\text{OH}$ (X is halogen atom such as Cl, Br, n is integral number of 2 to 12) is reacted for etherization with 4-hydroxyphenyl 4-hydroxy benzoate expressed by formula (2) on page 4, and the compound expressed by general formula (3) on page 4 is obtained. (in the formula, n is 2 to 12)

Next, the compound of general formula (3) obtained above and an isocyanate alkyl(metha)acrylate expressed by general formula (4) on page 2 or (metha)acrylate chloride are reacted, and the compound expressed by general formula (I) of this invention is obtained. (in the formula (4), R_2 is $-\text{H}$ or $-\text{CH}_3$, and m is integral number between 2 to 4.)

The above method is going to be explained more specifically in the following. First, the compound of general formula (2) is reacted with reactants such as KOH, K_2CO_3 , $NaOC_2H_5$ in an appropriate solvent such as alcohol, ether, acetone, or dimethylformamide to make sodium or potassium salt. Next, an alcohol halide expressed by general formula (1) is added, and the ether reaction is done, and the compound of general formula (3) is obtained. Also, the compound (3) and (metha)acrylate chloride or isocyanate alkyl (metha)acrylate expressed by the above general formula (4) are reacted in an appropriate solvent in the presence of a basic catalyst such as pyridine or triethylamine. After that, by repeating recrystallization using an appropriate solvent, the compound of the above general formula (I) of this invention can be obtained.

(effects of this invention)

The bi-functional (metha)acrylate of this invention is a new compound. This compound has phenyl ester benzoate which is a mesogen group in its molecular structure, and since it has flexible construction at both ends, the mutual function between monomers is strong. Depending on the length of alkylene, it shows liquid crystal behavior. Because of that, the (metha)acrylate itself expressed by general formula (I) will have superior strength if polymerized singly. Also, it shows superior characteristic after co-polymerizing it with other monomers as a reactive dilution agent. Especially, the (metha)acrylate of this invention can be used favorably for dental filling material by mixing inorganic filling agents and radical polymerization initiators. In such a case, an improvement in strength of 20 % or more compared to former dental filling material can be expected.

(examples of practice)

The following examples of practice are used to explain this invention more specifically. However, this invention is not limited to these examples of practice.

example of practice 1

2.3 g of 4-hydroxyphenyl 4-hydroxy benzoate (0.01 mol), 40 ml of acetone, and 1.38 g of potassium carbonate were added to a 100ml flask. While nitrogen was introduced, it was refluxed for 3 hours. After that, 4.0 g of 6-brom 1-hexanol (0.022 mol) was titrated taking 1 hour, and it was refluxed again for another 30 hours. After it was neutralized with hydrochloric acid, it was precipitated by adding a large amount of water, and the collected solid was recrystallized using methanol, and 1.42 g of a white crystal (will be called compound a) was obtained. The yield was 33 %.

Next, 4.3 g of compound a (0.01 mol), 1.58 g of pyridine (0.02 mol), and 40 ml of tetrahydrofuran were added to another 100 ml flask. While it was stirred, 2.18 g of chloride acrylate (0.022mol) was titrated gradually at room temperature. After it was stirred at room temperature for 1 hour, the temperature was raised gradually, and it was refluxed for 3 hours. After the reaction liquid was filtered to remove tetrahydrofuran, the remaining solid was recrystallized using isobutyl alcohol. 1.8 g of white crystal with the following structure was obtained. The yield was 33.5 %.

According to the infrared absorption spectrum of the reaction products, the absorption based on -OH near 3400 cm^{-1} was lost, and the carbonyl group of

5

methacrylate and absorption of C=C were observed at 1718 cm^{-1} and 1636 cm^{-1} , and the absorption of the carbonyl group bonded directly to the phenyl group was observed at 1730 cm^{-1} .

Analysis result according to $^1\text{H-NMR}$ is going to be shown in the following.
(see formula in page 5)

- (a) + (b) = 5.82 to 6.41 ppm (multi plette, 6H)
(c) + (e) = 3.97 to 4.33 ppm (multi plette, 8H)
(f) + (g) = 6.89 to 8.21 ppm (tetra plette, 8H)

Results of the elemental analysis were as follows.

table 1

elemental analysis

measured value

theoretical value

C

0.7008

0.6913

H

0.0690

0.711

Also, a molecular ion peak at $m/e = 538$ was observed by mass spectrum analysis.

From the above result, the reaction products were confirmed to be the compound expressed by the structural formula on page 5.

example of practice 2

4.30 g of compound a synthesized in example of practice 1 (0.01 mol), 1.58 g of pyridine (0.02 mol), and 40 ml of tetrahydrofuran were added to a 100 ml flask. While it was stirred, 2.30 g of chloride methacrylate (0.022 mol) was titrated gradually at normal temperature. After it was stirred at room temperature for 1 hour, the temperature was raised gradually, and it was refluxed for 3 hours. After the reaction liquid was filtered to remove tetrahydrofuran, the remaining solid was recrystallized using isobutyl alcohol. 2.32 g of white crystal with the following structure was obtained. The yield was 40.8 %.

Analysis result according to $^1\text{H-NMR}$ is going to be shown in the following.

(see formula in page 6 in top)

(a) = 5.69, 6.07 ppm (doublet, 4H)

(b) = 1.91 ppm (singlet, 6H)

(c) + (e) = 4.07 to 4.36 ppm (multiplette, 8H)

(d) = 1.52 to 1.80 ppm (multiplette, 16H)

(f) + (g) = 7.04 to 8.22 ppm (tetraplette, 8H)

Result of the elemental analysis was as follows.

table 2

elemental analysis

measured value

theoretical value

C

0.7133

0.6994

0.

0.

A molecular ion peak at $m/e =$ was also observed by mass spectrum analysis.

From the above result, the reaction product was confirmed as the compound expressed by the structural formula on the top of page 6.

example of practice 3

2.3 g of 4-hydroxyphenyl 4-hydroxy benzoate (0.01 mol), 40 ml of acetone, and 1.38 g of potassium carbonate were added to 100ml flask. While nitrogen was introduced, it was refluxed for 3 hours. After that, 5.3 g of 10-brom 1-octanol (0.022 mol) was titrated taking 1 hour, and it was refluxed again for another 30 hours. After it was neutralized with hydrochloric acid, it was precipitated by adding a large amount of water, and the remaining solid was recrystallized using methanol, and 2.1 g of a white crystal was obtained. The yield was 38.9 %.

Next, 5.4 g of this white crystal (0.01 mol), 1.58 g of pyridine (0.02 mol), and 40 ml of tetrahydrofuran were added to another 100 ml flask. While it was stirred, 2.18 g of chloride methacrylate (0.022mol) was titrated gradually at room temperature. After it was stirred at room temperature for 1 hour, the temperature was raised gradually, and it was refluxed for 3 hours. After the reaction liquid was filtered to remove tetrahydrofuran, the remaining solid was recrystallized using isobutyl alcohol. 3.6 g of a white crystal with the following structure was obtained. The yield was 66.9 %.

An infrared absorption spectrum showed the same absorption as in example of practice 1.

The results of the $^1\text{H-NMR}$ analysis is shown in the following.

see formula at the bottom of page 6

(a) = 5.71, 6.13 ppm (doublet, 4H)

(c) + (e) = 4.04 to 4.42 ppm (multiple, 8H)

(f) + (g) = 7.02 to 8.41 ppm (tetraplette, 8H)

The elemental analysis results are shown in the following.

table 3

elemental analysis

measured value

theoretical value

	C
measured value	0.7481
theoretical value	0.7430

0.
0.

A molecular ion peak at $m/e = 662$ was also observed by mass spectrum analysis.

From the above result, the reaction product was confirmed as the compound expressed by the structural formula on the bottom of page 6.

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PAGE 14

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(12) 公開特許公報 (A)

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特開平5-178794

(48)公開日 平成5年(1993)7月20日

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269/02		6917-4H		
271/16		6917-4H		
C 08 F 20/30	MMV	7242-4 J		
/ C 08 F 299/06	MRX	7442-4 J		

審査請求 衆議院 請求項の改訂(全 7 頁)

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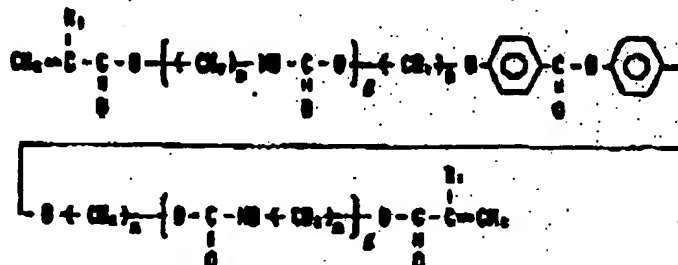
(54) 【発明の名称】 2官能(メタ)アクリレート

(57) 【要約】 .

●【構成】 一機一式

【目的】 新規なラジカル重合性の2官能(メタ)アクリレートを提供する。

【化1】



(式中、R₁はH又はCH₃、lは0又は1、mは2～4、nは2～12である)で表される2官能(メタ)ア

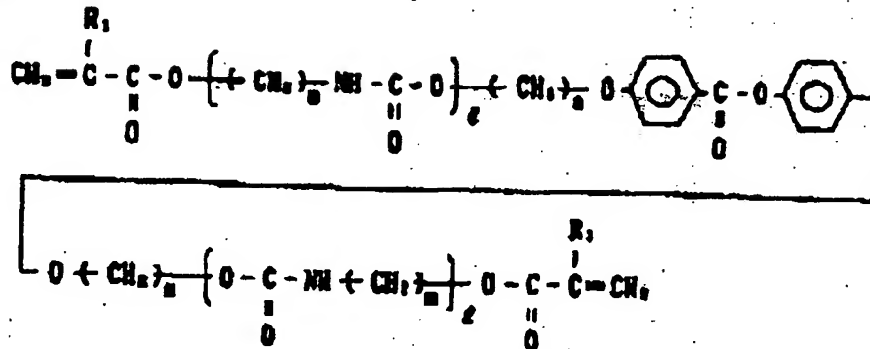
クリレート化合物である。

(2)

特開平5-178704

【特許請求の範囲】

【請求項1】 一般式、



(式中R₁ は-H又は-CH₃、lは0又は1、mは2～4、nは2～12である) で示される2官能(メタ)アクリレート。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、新規な2官能(メタ)アクリレートに関する。

【0002】

【従来の技術】 従来より重合体又は共重合体の原料に供される種々の多官能(メタ)アクリレートモノマーが知られている。例えば、ヘキサジオール(メタ)アクリレート、ネオペンチルグリコールジ(メタ)アクリレート、ポリエチレングリコールジ(メタ)アクリレート、ポリプロピレングリコールジ(メタ)アクリレート、グリセリントリ(メタ)アクリレート、トリメチロールプロパントリ(メタ)アクリレート、ペンタエリスリトールトリ(メタ)アクリレート、ジペンタエリスリトールヘキサ(メタ)アクリレート等の脂肪族系(メタ)アクリレート或いはビスフェノールAグリシジルジ(メタ)アクリレート、エチレンオキサイド変性ビスフェノール系

系Aジ(メタ)アクリレート、等の芳香族系(メタ)アクリレート等が公知である。

【0003】 これらの脂肪族系或いは芳香族系(メタ)アクリレートは一般に電子部島材料、光学材料、歯科材料、各種高分子の架橋材料として用いられる。しかしながら、脂肪族系(メタ)アクリレートは一般に重合性に優れたもののその重合体は物理強度、耐久性が十分でない等の問題を有しており、また芳香族系(メタ)アクリレートは、脂肪族系(メタ)アクリレートと比較してこれらの物性に優れた重合体を提供するがなお十分に満足されるものでない。

【0004】

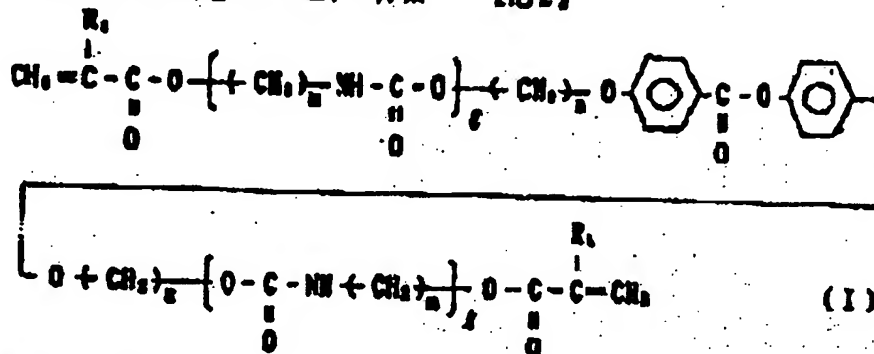
【発明が解決しようとする課題】 本発明は上記問題に鑑み、物理的強度、耐久性に優れた重合体を提供するための材料を得ることを目的とする。

【0005】

【課題を解決するための手段】 即ち本発明は一般式(1)、

【0006】

【化2】



(1)

式(1)で示されるものであるが、特に好適なものを更に具体的に示すと次の化合物である。

【0009】

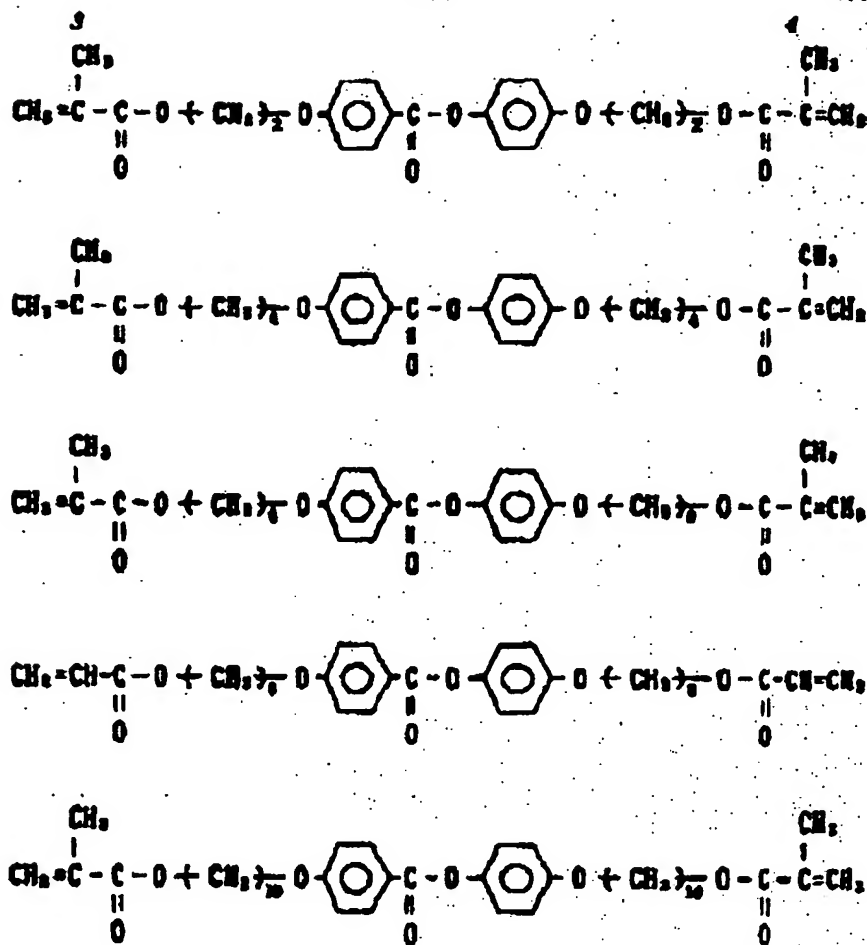
【化3】

【0007】 (式中R₁ は-H又は-CH₃、lは0又は1、mは2～4、nは2～12である) で示される2官能(メタ)アクリレートである。

【0008】 本発明の(メタ)アクリレートは上記一般

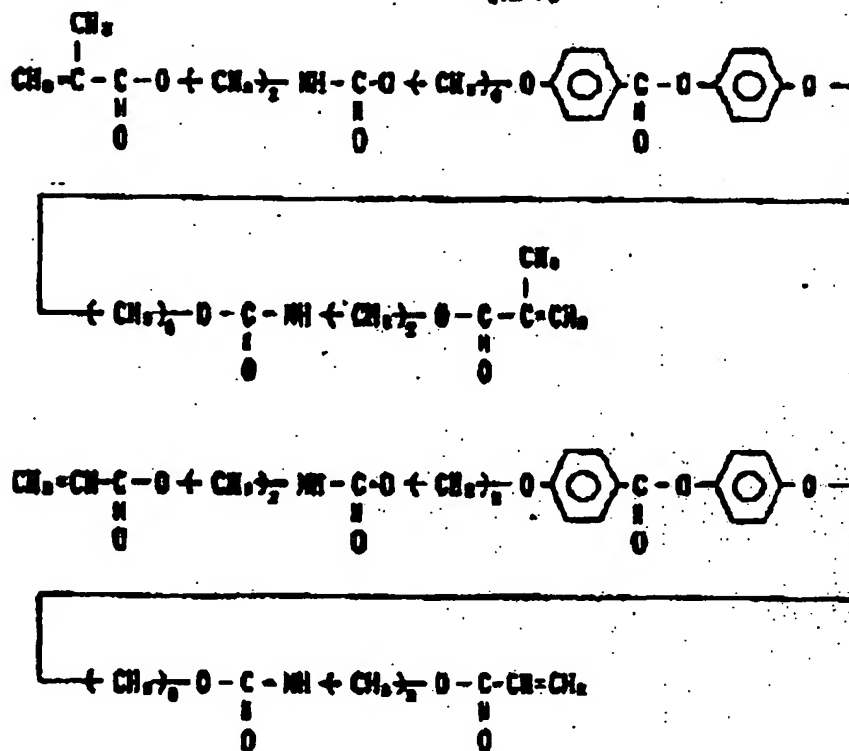
(3)

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[0010]

* * [化4]



[0011]である。

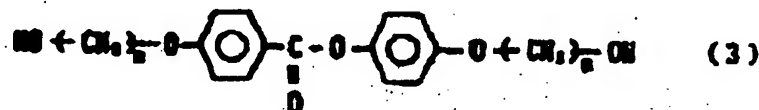
一般に次の (a) ~ (d) のような手段で一般式 (I)

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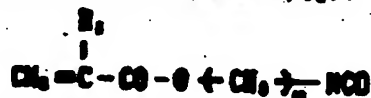
NOc1ccc(cc1)C(=O)c2ccc(cc2)O

【化·5】

(2)



【化6】



(4)

100251

【実施例】本発明を更に具体的に説明するため以下実施例を挙げて説明するが本発明はこれらの実施例に限定さ

【0026】実施例1

100mlのナス型フラスコに4-ヒドロキシフェニル4-ヒドロキシ安息香酸2.3g (0.01 mol)、アセトン40ml、炭酸カリウム1.38gを加え、塩酸を導入しながら3時間還流した。その後6-ブロム1-ペキサノール4.0g (0.022 mol)を1時間かけて滴下し、さらに30時間還流した。塩酸で中和した後、多量の水を加えて沈降させ、回収した固体をメタノールにより再結晶して1.42gの白色結晶（以下単に化合物aと言う）を得た。収率は、33%であった。

【0027】別に用意した100mlのナス型フラスコに化合物a 4.3g (0.01 mol)とピリジン1.58g (0.02 mol)、テトラヒドロフラン40mlを加え、攪拌しながら室温にてアクリル酸クロライド2.1g (0.022 mol)を徐々に滴下した。室温で1時

(5)

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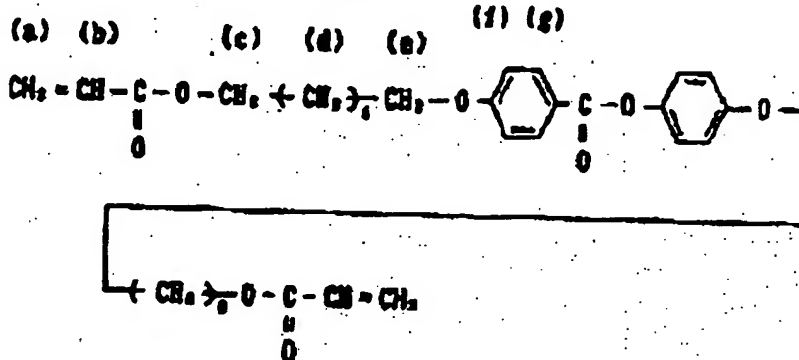
*同様にした後徐々に温度を上げ3時間還流した。反応液を減圧し、テトラヒドロフランを除去した後得られた固体をイソブチルアルコールにより再結晶することにより以下の構造を示す白色結晶1.8gを得た。収率は、33.5%であった。

【0028】得られた反応生成物の赤外吸収スペクトルによれば3400 cm^{-1} 付近の-OHに基づく吸収が消失し、メタクリレートのカルボニル基及びC=Cの吸収が1718 cm^{-1} と1636 cm^{-1} にフェニル基に直接結合したカルボニル基の吸収が1730 cm^{-1} に観察された。

【0029】 $^1\text{H-NMR}$ による分析結果を以下に示す。

【0030】

【化7】



【0031】(a) + (b) = 5.82~6.41ppm (マルチプレット, 6H)

(c) + (e) = 3.97~4.33ppm (マルチプレット, 8H)

(d) = 1.41~1.98ppm (マルチプレット, 16H)

(f) + (g) = 6.89~8.21ppm (テトラプレット, 8H)

元素分析の結果は以下に示す通りであった。

【0032】

【表1】

分析元素	C	H
実測値	0.7008	0.0690
理論計算値	0.6919	0.0711

【0033】また生成物の質量分析スペクトルにより $m/e=838$ の分子イオンピークが観察された。

【0034】以上の結果より、目的生成物が上記構造式で示される化合物であることが確認出来た。

【0035】実施例2

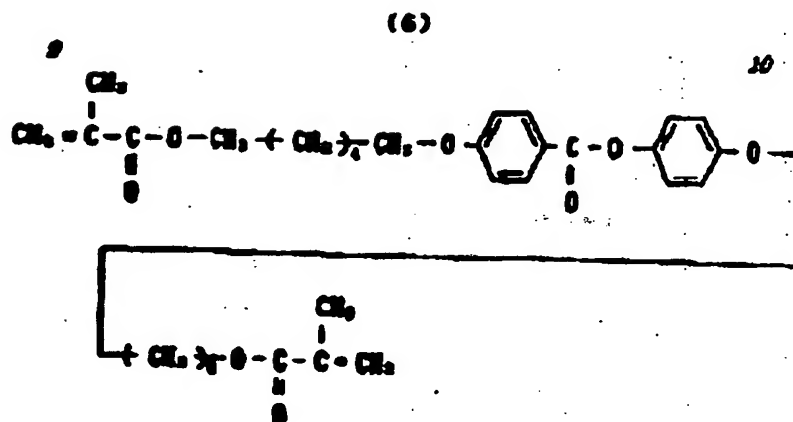
100mlのナス型フラスコに実施例1で合成した化合物a 4.30g (0.01 mol)とピリジン1.58g (0.02 mol)、テトラヒドロフラン40mlを加え、攪拌しながら室温にてメタクリル酸クロライド2.30g (0.022 mol)を徐々に滴下した。室温で1時間攪拌した後徐々に温度を上げ3時間還流した。反応液を減圧し、テトラヒドロフランを除去した後得られた固体をイソブチルアルコールにより再結晶することにより下記の構造を示す白色結晶2.32gを得た。収率は、40.8%であった。

【0036】この生成物の赤外吸収スペクトルは実施例1と同様な吸収を示した。

【0037】 $^1\text{H-NMR}$ による分析結果を以下に示す。

【0038】

【化8】



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【0039】 (a) = 5. 69, 6. 07 ppm (ダブルット, 4H)
(b) = 1. 91 ppm (シングレット, 6H)
(c) + (e) = 4. 07 ~ 4. 36 ppm (マルチブレット, 8H)
(d) = 1. 52 ~ 1. 80 ppm (マルチブレット, 16H)

(f) + (g) = 7. 04 ~ 8. 22 ppm (テトラブレット, 8H)

元素分析の結果は以下に示す通りであった。

【0040】

【表2】

分析元素	C	H
実 測 値	0.7133	0.0712
理論計算値	0.6904	0.0767

【0041】 また、生成物の質量分析スペクトルにより $m/e =$ の分子イオンピークが観察された。

【0042】 以上の結果より、目的生成物が上記構造式で示される化合物であることが確認された。

【0043】 実施例3

* 100mlのナス型フラスコに4-ヒドロキシフェニル4-ヒドロキシ安息香酸2.3g (0.01 mol)、アセトン40ml、炭酸カリウム1.38gを加え、溶液を導入しながら3時間還流した。その後10-ブROM1-オクタノール5.3g (0.022 mol)を1時間かけて滴下し、さらに30時間還流した。塩酸で中和した後、多量の水を加えて沈澱させ、懸濁した結晶をメタノールにより再結晶して2.1gの白色結晶を得た。収率は、38.9%であった。

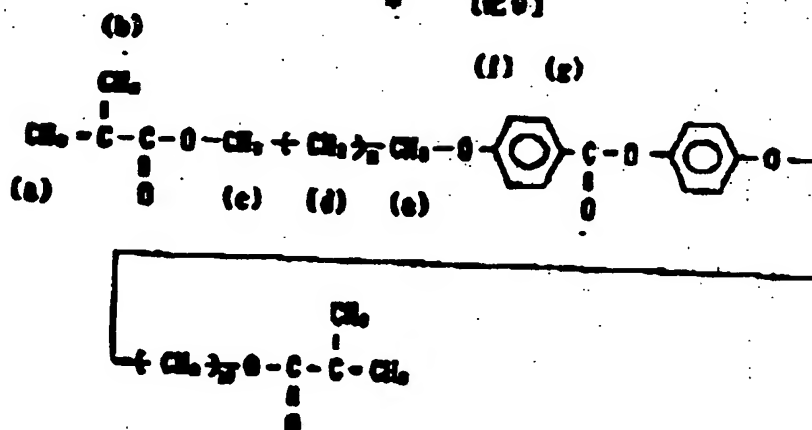
【0044】 別に用意した100mlのナス型フラスコに得られた白色結晶5.4g (0.01 mol)とピリジン1.68g (0.02 mol)、テトラヒドロフラン40mlを加え、攪拌しながら室温にてメタクリル酸クロライド2.18g (0.022 mol)を徐々に滴下した。室温で1時間攪拌した後徐々に温度を上げ3時間還流した。反応液を蒸留し、テトラヒドロフランを除去した後得られた固体をイソブチルアルコールにより再結晶することにより以下の構造を示す白色結晶3.6gを得た。収率は、66.9%であった。

【0045】 この生成物の赤外線吸収スペクトルは実施例1と同様な吸収を示した。

【0046】 $^1\text{H-NMR}$ による分析結果を示す。

【0047】

【表3】



【0048】 (a) = 5. 71, 6. 13 ppm (ダブルット, 4H)

(c) + (e) = 4. 04 ~ 4. 42 ppm (マルチブレット, 8H)

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(f) + (g) = 7.02 ~ 8.41 ppm (テトラプレット, 8H)

また生成物の元素分析結果を以下に示す。

【0049】

【表3】

分析元素	C	H
実測値	0.7481	0.8503
理論計算値	0.7430	0.8639

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【0050】また生成物の質量分析スペクトルによりm/e=662の分子イオンピークが観察された。

【0051】以上の結果より、目的生成物が上記構造式で示される化合物であることを確認した。

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